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PATENT ABSTRACTS OF JAPAN

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(54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a nonaqueous electrolyte secondary battery with a long cycle life by containing a mixture of flake graphite and fibrous carbon as a conductor in a positive electrode.

SOLUTION: A nonaqueous electrolyte secondary battery is constituted with a negative electrode mainly comprising a carbon material (graphite material or the like) capable of doping/undoping lithium, a positive electrode, and a nonaqueous electrolyte prepared by dissolving an electrolyte in a nonaqueous solvent. The positive electrode contains a positive mix comprising a positive active material (lithium transition metal compound oxide), a mixture of flake graphite and fibrous carbon, and a binder (polyvinylidene fluoride or the like). The content of the mixture of flake graphite and fibrous carbon contained in the positive mix is 3-16wt.%, and the mixing ratio of flake graphite and fibrous carbon is 85:15 to 25:75. The nonaqueous electrolyte secondary battery with long cycle life and in which the electrode structure of the positive electrode is not broken even when the battery is used in heavy load discharge condition can be obtained.

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CLAIMS

[Claim(s)]

[Claim 1] The nonaqueous electrolyte rechargeable battery characterized by the mixture of a scale-like graphite and fibrous carbon containing as an electric conduction agent in the above-mentioned positive electrode in the nonaqueous electrolyte rechargeable battery which comes to have nonaqueous electrolyte which comes to dissolve an electrolyte in the negative electrode, positive electrode, and non-aqueous solvent which make a subject the carbon material which can dope and ** dope a lithium.

[Claim 2] The nonaqueous electrolyte rechargeable battery according to claim 1 with which the mixed ratio of a scale-like graphite and fibrous carbon contained in a positive electrode is characterized by being 85:15-25:75 in a weight ratio.

[Claim 3] the positive electrode where a positive electrode consists of the mixture and the binding material of a positive active material, a scale-like graphite, and fibrous carbon -- a mixture -- having -- becoming -- a positive electrode -- the nonaqueous electrolyte rechargeable battery according to claim 1 characterized by the content of the mixture of the scale-like graphite contained in a mixture and fibrous carbon being 3 - 16 % of the weight

[Claim 4] The nonaqueous electrolyte rechargeable battery according to claim 1 characterized by the lithium transition-metals multiple oxide expressed with LiMO_2 (however, M expresses at least one sort of Co, nickel, Mn, Fe, aluminum, V, and Ti) to a positive electrode as a positive active material containing.

[Claim 5] The carbon material of a negative electrode is a nonaqueous electrolyte rechargeable battery according to claim 1 characterized by being graphite material.

[Claim 6] The carbon material of a negative electrode is a nonaqueous electrolyte rechargeable battery according to claim 1 characterized by being nongraphitizing-carbon material.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] Especially this invention relates to improvement of the electric conduction agent used for a positive electrode about a nonaqueous electrolyte rechargeable battery.

[0002]

[Description of the Prior Art] Remarkable progress of electronic technology in recent years is making small [of electronic equipment], and lightweight-ization realize one after another. In connection with it, it is increasingly called for also from the cell as a power supply for portable small and that they are lightweight and high-energy density.

[0003] Conventionally, as a rechargeable battery of a general use, solution system rechargeable batteries, such as a lead cell and a nickel cadmium battery, are in use. However, although it can be satisfied [with a cycle property] of these solution system rechargeable batteries to some extent, it cannot be said that it is enough in respect of a cell weight or an energy density.

[0004] On the other hand, research and development of the nonaqueous electrolyte rechargeable battery using a lithium or a lithium alloy as a negative-electrode material are done briskly recently. Especially by this cell, it is used as a positive-electrode material and has high-energy density, and self-discharge also has few high Li content multiple oxides of discharge voltage which is represented by LiCoO_2 , and they have the outstanding feature of being lightweight.

[0005] however, as for this nonaqueous electrolyte rechargeable battery, a charge-and-discharge cycle advances -- following -- the time of charge -- a negative-electrode top -- a lithium -- the shape of a dendrite -- a crystal growth -- carrying out -- just -- being alike -- possibility of having said that it arrived at a positive electrode and resulted in internal short-circuit is high. Moreover, since the crystal growth of the shape of this dendrite becomes so remarkable that charge and discharge become rapid, it is necessary to avoid rapid charge and discharge if possible. For this reason, the path to utilization must be called far thing.

[0006] Then, the nonaqueous electrolyte rechargeable battery (the so-called rechargeable lithium-ion battery) which used the carbon material as a negative-electrode material attracts attention further. This nonaqueous electrolyte rechargeable battery uses doping and ** doping a lithium between the carbon layers of a carbon material for a negative-electrode reaction, even if a charge-and-discharge cycle advances, the phenomenon in which a dendrite-like lithium deposits on a negative electrode is not accepted, but it has high-energy density, and the charge-and-discharge cycle property of having excelled while it was lightweight is demonstrated.

[0007] In such a nonaqueous electrolyte rechargeable battery, the carbon material with which, as for the carbon material which can be used as a negative-electrode material, various **** were first put in practical use as a negative-electrode material is a crystalline low carbon material obtained by heat-treating comparatively corks and nongraphitizing-carbon material, i.e., an organic material, such as a glassy carbon, at low temperature. The nonaqueous electrolyte rechargeable battery using the electrolytic solution which uses as the main solvent the negative electrode which consisted of these low crystallinity carbon materials, and a propylene carbonate (PC) is already commercialized.

[0008] Furthermore, recently, the graphites from which the crystal structure developed are used as a negative-electrode material.

[0009] These graphites were made difficult [the use as a negative-electrode material] in order to disassemble PC used widely as a main solvent of a non-aqueous solvent until now. However, it becomes clear by using an ethylene carbonate (EC) instead of PC that such un-arranging is canceled, and it can be used now for a negative electrode in the form combined with this EC.

[0010] A scale-like thing can receive graphites comparatively easily and it is conventionally used widely as an electric conduction agent for alkaline cells etc. These graphites have high crystallinity compared with a low crystallinity carbon material, and its true density is high. Therefore, if these graphites constitute a negative electrode, high electrode restoration nature will be obtained and the energy density of a cell will be raised. From this, it can be said that graphites

are the large material of expectation as a negative-electrode material.

[0011] Li content multiple oxide represented by LiCoO_2 as a positive-electrode material on the other hand is in use. Here, when using this Li content multiple oxide as a positive-electrode material, since the conductivity of this oxide itself is very small, usually electric conduction agents, such as a graphite, are used together. namely, the positive electrode where the positive electrode added the electric conduction agent further to Li content multiple oxide and binding material -- it is constituted as a mixture

[0012]

[Problem(s) to be Solved by the Invention] By the way, in the positive electrode using such a Li content multiple oxide, in order that the unit crystal lattice of this Li content multiple oxide may carry out expansion contraction on the occasion of charge and discharge, thickness change of an about [10%] arises at the maximum. Moreover, in order that the microcrystal of a carbon material may carry out expansion contraction on the occasion of charge and discharge also in a negative electrode, thickness change of an about [10%] arises at the maximum too.

[0013] If such thickness change arises in a positive electrode and a negative electrode, electrodes press each other and electrode structure may be gradually destroyed by this. Especially when electrode structure is destroyed, in a low positive electrode, degradation of a remarkable performance is invited for own conductivity of an active material. Especially electrode structural failure such has a large problem, when the use to the business use video camera, such as an object for broadcast, and the video camera with liquid crystal with which it becomes remarkable and a cell is used on heavy-loading electric discharge conditions for the bottom of a heavy-loading electric discharge condition, note type works SHON, etc. is considered.

[0014] Then, it is proposed in view of such the conventional actual condition, even when it uses on heavy-loading electric discharge conditions, electrode structure is not destroyed, but a cycle life is long and this invention aims at offering the nonaqueous electrolyte rechargeable battery with which high reliability is acquired.

[0015]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, as a result of this invention persons' inquiring wholeheartedly, it came to acquire knowledge that the cell in which a long cycle life is shown also in heavy-loading electric discharge conditions comes to be obtained by using the mixture of a scale-like graphite and fibrous carbon as an electric conduction agent of a positive electrode.

[0016] this invention is completed based on such knowledge.

[0017] That is, this invention is applied to the nonaqueous electrolyte rechargeable battery which comes to have nonaqueous electrolyte which comes to dissolve an electrolyte in the negative electrode, positive electrode, and non-aqueous solvent which make a subject the carbon material which can dope and ** dope a lithium.

[0018] the positive electrode where a positive electrode consists of a positive active material, an electric conduction agent, and binding material in such a nonaqueous electrolyte rechargeable battery -- it has a mixture, and is constituted and the mixture of a scale-like graphite and fibrous carbon is used as this electric conduction agent in this invention

[0019] If the mixture of a scale-like graphite and fibrous carbon is used as an electric conduction agent of a positive electrode, while conductivity will be given to a positive electrode by this scale-like graphite and fibrous carbon, fibrous carbon acts so that the electrode structure of a positive electrode may be held. Therefore, even when the electrode structural failure which happens by expansion contraction of the positive active material accompanying charge and discharge is suppressed, for example, charge and discharge are performed under heavy-loading electric discharge conditions, the performance of a positive electrode is not spoiled, but a long cycle life is acquired.

[0020] Here, it is appropriate for the mixed ratio of the scale-like graphite and fibrous carbon which are used as this electric conduction agent to be referred to as 85:15-25:75 by the weight ratio. moreover, a positive electrode -- a mixture -- 3 - 16 % of the weight is suitable for the content of the mixture of the scale-like graphite which is alike and receives the whole, and fibrous carbon

[0021] in addition, a positive electrode -- as a positive active material of a mixture, the lithium transition-metals multiple oxide expressed with LiMO_2 (however, M expresses at least one sort of Co, nickel, Mn, Fe, aluminum, V, and Ti), for example is used

[0022] On the other hand, a carbon material is used as an active material of a negative electrode. Graphite material and nongraphitizing-carbon material are mentioned as such a carbon material.

[0023]

[Embodiments of the Invention] Hereafter, the gestalt of concrete operation of this invention is explained.

[0024] The nonaqueous electrolyte rechargeable battery of this invention has nonaqueous electrolyte which comes to dissolve an electrolyte in the negative electrode, positive electrode, and non-aqueous solvent which make a subject the carbon material which can dope and ** dope a lithium, and is constituted.

[0025] the positive electrode which the above-mentioned positive electrode mixed a positive active material, an electric conduction agent, and binding material, and was prepared -- a mixture is distributed to an organic solvent -- making -- a

positive electrode -- a mixture -- it is obtained by considering as a slurry and carrying out compression molding of this [0026] this invention -- this positive electrode -- the mixture of a scale-like graphite and fibrous carbon is used as an electric conduction agent which a mixture is made to contain

[0027] This scale-like graphite is used as an electric conduction agent which gives conductivity from the former to an oxide etc., and since it is high crystallinity, electronic conductivity is very high. However, especially in the positive electrode using this scale-like graphite independent as an electric conduction agent, in the bottom of a heavy-loading electric discharge condition, electrode structure is destroyed by expansion contraction of the positive active material accompanying charge and discharge, and performance degradation is invited. Here, if fibrous carbon is added to such a positive electrode, this fibrous carbon will function as holding electrode structure, and the electrode structural failure accompanying charge and discharge will be suppressed. Moreover, if this fibrous carbon is compared with a scale-like graphite, although it is a little inferior, it also has the operation as an electric conduction agent which gives conductivity. Therefore, in the positive electrode using the mixture of a scale-like graphite and fibrous carbon as an electric conduction agent, having a performance equivalent to the conventional positive electrode, the electrode structural failure accompanying charge and discharge will be suppressed, and it will contribute to the reinforcement of a cell greatly.

[0028] As the above-mentioned scale-like graphite, the natural graphite specifically produced as an ore or an organic material is carbonized, and the artificial graphite compounded by carrying out high temperature processing further is mentioned.

[0029] Among these, a natural graphite is produced in China, Madagascar, Ceylon, Mexico, Brazil, etc. If many inorganic impurities other than a graphite are contained and especially the metallic element is mixing as an impurity in the state of an ore, this will be eluted electrochemically and will do a bad influence to a cell. For this reason, it is necessary to make it dissolve in a solvent and to flush these impurities. An organic system solvent is usable to the inorganic alkaline solution in which the solution in which inorganic acid solution and the inorganic organic acid in which hydrogen fluoride, the hydrogen chloride, etc. were included were included, caustic soda, etc. were included as this solvent, the solution in which the basic organic substance was included, and a pan.

[0030] On the other hand, an artificial graphite is generated by heat-treating an organic material. As an organic material used as this start raw material, coal and a pitch are typical.

[0031] There are what is obtained by operation of distillation (vacuum distillation, **** distillation, steam distillation), a heat polycondensation, extraction, a chemistry polycondensation, etc. from the tar obtained as a pitch by carrying out elevated-temperature pyrolysis of a coal tar, an ethylene bottom oil, the crude oil, etc., asphalt, etc., a pitch generated in addition to this at the time of wood dry distillation.

[0032] Furthermore, as a start raw material used as a pitch, there is a polyvinyl chloride resin, polyvinyl-acetate, polyvinyl butyrate, 3, and 5-dimethylphenol resin etc.

[0033] In the middle of carbonization, at a maximum of about 400 degrees C, these coal and a pitch are liquefied, exist, and if rings will be in condensation and the state where cyclized many and laminating orientation was carried out, by holding at the temperature and they become the temperature of about 500 degrees C or more after that, they will form a solid carbon precursor, i.e., a semicoke. Such a process is called liquid-phase-carbonization process, and it is a typical generation process of easily graphitized carbon.

[0034] In addition, the derivative is also still more nearly usable as condensation heterocyclic compounds, such as condensation polycyclic hydrocarbon compounds, such as naphthalene, a phenanthrene, an anthracene, triphenylene, a pyrene, a perylene, pen TAFEN, and pentacene, other derivatives (for example, these carboxylic acids, a carboxylic-acid anhydride, carboxylic-acid imide, etc.) or mixture, an acenaphthylene, an indole, an iso indole, a quinoline, an isoquinoline, a quinoxaline, a phthalazine, a carbazole, an acridine, a phenazine, and phenanthridine, and a raw material which is

[0035] In order to generate a desired artificial graphite by using the above organic material as a start raw material For example, after carbonizing the above-mentioned organic material at 300-700 degrees C among inert gas air currents, such as nitrogen It calcines among an inert gas air current on the about [holding-time 0-30 hour] conditions in the programming rate of per minute 1-100 degrees C, the attainment temperature of 900-1500 degrees C, and attainment temperature (that through which it passed to this process is a graphitizability carbon material), and 2000 more degrees C or more are preferably heat-treated above 2500 degrees C. Of course, depending on the case, you may omit carbonization and calcining operation.

[0036] In addition, let these natural graphites or an artificial graphite be a scale-like graphite by grinding and classifying. In order to acquire an ideal scale configuration at this time, it is desirable that C shaft microcrystal thickness of the field where a graphite has high crystallinity and is measured by X-ray diffraction analysis (002) is 100nm or more. In order to obtain more monotonous powder, this is separating from the carbon hex-steel side weakly combined with Van der Waals force, and is because it is more convenient to break the graphite concerned. Moreover, in

order to acquire conductivity high as an electric conduction agent, the one where crystallinity is higher is advantageous.

[0037] In this invention, fibrous carbon is used as an electric conduction agent combining such a scale-like graphite.

[0038] There is a vapor-growth carbon fiber obtained by growing up a carbon crystal by making a sink, an iron particle, etc. into a catalyst directly on what obtained by heat-treating the precursor which becomes fibrous carbon from the macromolecule by which spinning was carried out fibrous, or a pitch, and the base made with the temperature of about 1000 degrees C in organic substance steams, such as benzene.

[0039] When obtaining fibrous carbon with heat treatment, there are a polyacrylonitrile (PAN) and rayon as a precursor of a macromolecule system. Moreover, a polyamide, a lignin, polyvinyl alcohol, etc. are usable.

[0040] There are what is obtained by operation of distillation (vacuum distillation, atmospheric distillation, steam distillation), a heat polycondensation, extraction, a chemistry polycondensation, etc. from the tar obtained as a precursor of a pitch system by carrying out elevated-temperature pyrolysis of a coal tar, an ethylene bottom oil, the crude oil, etc., asphalt, etc., a pitch generated in addition to this at the time of wood dry distillation.

[0041] As a start raw material which furthermore serves as a pitch, there is a polyvinyl chloride resin, polyvinyl-acetate, polyvinyl butyrate, 3, and 5-dimethylphenol resin etc.

[0042] In addition, condensation multi-cyclization hydride, such as naphthalene, a phenanthrene, an anthracene, triphenylene, a pyrene, a perylene, pen TAFEN, and pentacene, other derivatives (for example, these carboxylic acids, a carboxylic-acid anhydride, carboxylic-acid imide, etc.). Or the derivative of condensation heterocyclic compounds, such as mixture, an acenaphthylene, Indore, an iso indole, a quinoline, an isoquinoline, a quinoxaline, a phthalazine, a carbazole, an acridine, a phenazine, and phenanthridine, and a further is also usable as a raw material of a pitch.

[0043] It becomes fibrous carbon by the precursor of a macromolecule system and the precursor of a pitch system being further heat-treated in an elevated temperature after that through the process of non-deliquesce or stabilization.

[0044] In addition, in case a macromolecule etc. is carbonization, the process of non-deliquesce [this] or stabilization is a process which oxidizes a fiber front face using an acid, oxygen, ozone, etc., as neither melting nor a pyrolysis is caused. Under the present circumstances, an art can be suitably chosen according to the kind of precursor. However, processing temperature needs to choose below the melting point of a precursor. Moreover, multiple-times processing is repeated if needed and stabilization may fully be made to be performed.

[0045] In order to obtain fibrous carbon, after carbonizing the precursor of the macromolecule system to which this non-deliquesce or stabilization was performed, or the precursor of a pitch system at the temperature of 300-700 degrees C among inert gas air currents, such as nitrogen, it is obtained by calcining among an inert gas air current on the about [holding-time 0-30 hour] conditions in the programming rate of per minute 1-100 degrees C, the attainment temperature of 900-1500 degrees C, and attainment temperature. Of course, depending on the case, you may omit carbonization.

[0046] Any are sufficient as long as it is the organic substance which may become gas-like as a start raw material on the other hand when obtaining a carbon fiber by the vapor growth. For example, what exists according to the shape of a gas in ordinary temperature, such as ethylene and a propane, the thing evaporated by giving bubbling etc. at a room temperature like benzene, or the organic substance which can carry out heating evaporation at the temperature below pyrolysis temperature is usable.

[0047] The crystal growth of the vaporized organic substance is carried out as fibrous carbon by being emitted on a direct hot base. The temperature in this case has 400 degrees C - desirable about 1500 degrees C, and it is suitably chosen by the kind of organic substance which is a start raw material. Moreover, the kind of base has a quartz, desirable nickel, etc. and is suitably chosen by the kind of organic substance which is a start raw material too.

[0048] In order to promote a crystal growth, you may make it use a catalyst at this time. As a catalyst, that which atomized iron, nickel or its mixture, etc. is usable, in addition the metal called a graphitization catalyst and its oxide also function as a catalyst. These catalysts are selectable suitably by the kind of organic substance which is a start raw material.

[0049] In addition, the obtained fibrous carbon may be made to carry out graphitization processing among an inert gas air current on the about [holding-time 0-30 hour] conditions in 2500 degrees C or more and attainment temperature preferably further the programming rate of per minute 1-100 degrees C, and the attainment temperature of 2000 degrees C or more. Thereby, the function as the increase of electronic conductivity and an electric conduction agent improves.

[0050] Moreover, as for the obtained fibrous carbon, what ground according to the thickness of an electrode, the particle size of an active material, etc., and you may make it present an electric conduction agent, and became a single fiber at the time of spinning is usable as an electric conduction agent. In addition, you may perform pulverization by any between the temperature up process before and after carbonization and calcining or before graphitization.

[0051] Although an electric conduction agent mixes above scale-like graphites and above fibrous carbon and it is constituted, as for the mixed ratio of a scale-like graphite and fibrous carbon, 85:15-25:75 are desirable, and 80:20-

30:70 are more desirable. When the ratio of a scale-like graphite is less than this range, conductivity may be insufficient, and when fibrous carbon is less than this range, the operation holding electrode structure is not fully obtained. moreover, the positive electrode of an electric conduction agent -- the addition to a mixture -- a positive electrode -- a mixture -- it is desirable that it is 3-16 % of the weight to the whole, and it is more desirable that it is 4-10 % of the weight. When there are few additions of an electric conduction agent than this range, the operation which gives conductivity, and the operation holding electrode structure are not fully obtained. Moreover, when there are more additions of an electric conduction agent than this range, the rate of the part positive active material decreases, and it leads to the fall of capacity.

[0052] in addition, a positive electrode -- each thing usually used with this kind of nonaqueous electrolyte rechargeable battery as the other materials used for a mixture, i.e., a positive active material, and binding material is usable

[0053] For example, it is desirable that Li of sufficient amount is included as a positive active material, for example, the intercalation compound containing the compound metallic oxide which consists of a lithium expressed with a general formula LiMO_2 (however, M expresses at least one sort of Co, nickel, Mn, Fe, aluminum, V, and Ti.) and transition metals, or Li etc. is suitable.

[0054] Since it aims at that especially this invention attains high capacity, a positive electrode needs to include Li of charge-and-discharge capacity of 250 or more mAh(s) of 1g this ** of negative-electrode carbonaceous material at a steady state (for example, after repeating charge and discharge about 5 times), and it is more desirable that Li of charge-and-discharge capacity of 300 or more mAhs is included. In addition, Li does not necessarily need to be altogether supplied from positive-electrode material, and, in short, Li of charge-and-discharge capacity of 250 or more mAhs per carbonaceous material 1g should just exist in a fuel cell subsystem. Moreover, suppose that this amount of Li is judged by measuring the service capacity of a cell.

[0055] Moreover, as binding material, since it excels in solvent resistance, fluorine system resins, such as a polyvinylidene fluoride, are suitable.

[0056] the negative electrode which the negative electrode mixed a negative-electrode active material and binding material, and was prepared on the other hand -- a mixture is distributed to an organic solvent -- making -- a negative electrode -- a mixture -- it considers as a slurry and is obtained by pressing this

[0057] The carbon material as a negative-electrode active material which can dope and ** dope a lithium ion can be used. As a carbon material, although each of graphite material, graphitizability carbon materials, and nongraphitizing-carbon material is selectable, when especially graphite material is used for a negative electrode, this invention demonstrates a big effect.

[0058] The material which shows the physical-properties parameter of the spacing of a field (002) setting to 0.37nm or more, and true density setting to the differential thermal analysis (DTA) in the inside of 1.70 g/cm less than 3 and air, and not having an exoergic peak in 700 degrees C or more as a nongraphitizing-carbon material is suitable.

[0059] As a representative of nongraphitizing-carbon material, the furan resin which consists of copolymerization with furfuryl alcohol or the homopolymer of a furfural, a copolymer, and other resins is calcinated, and there are some which carbonized.

[0060] Furthermore, as an organic material used as a start raw material, conjugated-system resins, such as phenol resin, acrylic resin, halogenation vinyl resin, polyimide resin, a polyamidoimide resin, polyamide resin, a polyacethylene, and poly (p-phenylene), a cellulose and its derivative, and arbitrary organic macromolecule system compounds can be used.

[0061] Moreover, finally it becomes nongraphitizing-carbon material in the state of solid phase like [what introduced the functional group which contains oxygen in the petroleum pitch which has a specific H/C atomic ratio (the so-called oxygen bridge formation)] the aforementioned furan resin, without fusing in process of carbonization (400 degrees C or more).

[0062] Here, a petroleum pitch is obtained by operation of distillation (vacuum distillation, atmospheric distillation, steam distillation), a heat polycondensation, extraction, a chemistry polycondensation, etc. from tar, asphalt, etc. which are obtained by elevated-temperature pyrolyses, such as a coal tar, an ethylene bottom oil, and a crude oil. At this time, the H/C atomic ratio of a petroleum pitch is important, and in order to obtain a nongraphitizing carbon, it is necessary to set this H/C atomic ratio to 0.6-0.8.

[0063] Although a concrete means to introduce the functional group which contains oxygen in these petroleum pitches is not limited, the wet method by solution, such as a nitric acid, a mixed acid, a sulfuric acid, and a hypochlorous acid, or the dry process by the oxidizing gas (air, oxygen), the reaction according further to solid reagents, such as sulfur, nitric-acid ammonia, persulfuric-acid ammonia, and a ferric chloride, etc. are used, for example. Although especially oxygen content is not limited, as shown in JP,3-252053,A, it is 5% or more still more preferably 3% or more preferably. the conditions that this oxygen content does not have an exoergic peak for the spacing of a field (002) in 700 degrees C or more in DTA in the inside of 0.37nm or more and an air air current when the crystal structure of the

carbon material finally obtained is affected and oxygen content is made into this range -- filling -- negative-electrode capacity -- size -- it becomes a thing

[0064] Moreover, the compound which makes a principal component Lynn indicated by JP,3-137010,A, oxygen, and carbon also shows the same physical-properties parameter as the aforementioned nongraphitizing-carbon material, and is usable as a negative-electrode active material.

[0065] Furthermore, if it becomes a nongraphitizing carbon through solid-phase-carbonization process about all other organic materials by oxygen bridge formation processing etc., it is usable as a start raw material. In addition, the art for performing this oxygen bridge formation is not limited.

[0066] What is necessary is just to calcinate programming-rate per minute on the about [holding-time 0-30 hour] conditions in 1-100 degree C, attainment temperature 900-1300 degree C, and attainment temperature, after carbonizing at the temperature of 300-700 degrees C in order to use the above organic material for a start raw material and to compound a carbon material for example. Of course, depending on the case, you may omit carbonization operation.

[0067] Although negative-electrode material is presented because the obtained carbon material grinds and classifies, you may perform this pulverization by any between the temperature up process before and after carbonization, calcining, and elevated-temperature heat treatment.

[0068] Next, the graphite material used as a negative electrode is explained.

[0069] As a graphite material, it is desirable that true density is three or more 2.1g/cm, and it is more desirable that it is more than 2.18 g/cm<sup>³.

[0070] In order to obtain such true density, it is required for less than 0.340nm of spacings of the field acquired with an X-ray diffraction method (002) to be 0.335nm or more and 0.337nm or less still more preferably, and for C shaft microcrystal thickness of a field (002) to be 14.0nm or more.

[0071] Furthermore, the G value in the Raman spectrum used as the index of a structure defect micro as a crystal structure parameter is also important. G value is expressed with the ratio of the integrated intensity of the signal originating in the graphite structure in a carbon material, and the integrated intensity of the signal originating in amorphous structure, and serves as an index of a micro crystal structure defect. As for this G value, 2.5 or more are desirable. When G value is less than 2.5, three or more 2.1g/cm true density may not be obtained.

[0072] Moreover, in order to carry out reinforcement of the cycle life of a cell, the average (average shape-parameter xave) and specific surface area of the relative bulk density of a graphite and a shape parameter x are important.

[0073] That is, as for the relative bulk density of graphite material, it is desirable that they are three or more 0.4 g/cm from a viewpoint which attain long cycle-life-ization. if relative bulk density constitutes a negative electrode using three or more 0.4 g/cm graphite material -- a negative electrode -- a mixture -- the good negative electrode of the electrode structure where graphite material separates and does not fall from a layer is obtained, and the cycle life of a cell extends In addition, the more desirable range of relative bulk density is three or more further 0.6 g/cm three or more 0.5 g/cm.

[0074] Furthermore, in order to acquire a long cycle life, while relative bulk density is this range, it is desirable for the average of a shape parameter x shown by the following formula to use the graphite powder not more than 125.

[0075] $x = (W/T) \times (L/T)$

x: shape-parameter T: -- powdered partial thickness L: with the thinnest thickness -- length W: of the powdered direction of a major axis -- the length of the direction which intersects perpendicularly with a powdered major axis, i.e., the typical configuration of a graphite powder, is shown in [drawing 1](#) and [drawing 2](#) -- the time -- a flat approximate circle -- it has the shape of pillar-shaped or an abbreviation rectangular parallelepiped

[0076] the time of setting to W the length of the direction which intersects perpendicularly the thickness of the portion with the thinnest thickness of this graphite powder with T and the major axis which is equivalent to L and depth in the length of a portion with the longest length -- L and W -- the product of ** which ** (ed) each by T is the aforementioned configuration rose meter x It means that the height to an area of base is high, and the degree of flatness is small, so that this shape parameter x is small.

[0077] Average shape-parameter xave is the average of this shape parameter x, and it asks as follows. First, graphite sample powder is observed using SEM (scanning electron microscope), and the portion with the longest length of a particle chooses ten particles which are **30% of the mean particle diameters measured using particle-size-distribution measuring devices, such as a laser diffraction method. And a shape parameter x is calculated about each of ten selected powder, and the average is computed.

[0078] The negative electrode constituted using the graphite powder this average shape-parameter xave of whose relative bulk density is above-mentioned within the limits, and is less than [125] has good electrode structure, and a longer cycle life is acquired. In addition, the still more desirable range of average shape-parameter xave is 00 or less [two or more 1] more preferably five or less [1-1. / 2 or more].

[0079] Moreover, if the graphite powder whose specific surface area is below 9m²/g is used in addition to satisfying

the above conditions, the cycle life of a cell will extend further. That is, by the graphite powder, usually, the particle of submicron level has adhered and it is thought that this particle has influenced the fall of the relative bulk density of a graphite powder. The specific surface area of a graphite powder becomes the index of the grade of adhesion of a particle from a bird clapper here at such a big value that an adhering particle increases. Like below $9\text{m}^2/\text{g}$, the graphite powder with a comparatively small specific surface area has little adhesion of a particle, and big relative bulk density is obtained. Therefore, the cycle life of a cell will extend. In addition, as for this specific surface area, it is more desirable that it is below $7\text{m}^2/\text{g}$, and it is still more desirable that it is below $5\text{m}^2/\text{g}$.

[0080] Moreover, in order to acquire safety and reliability high as a practical use cell, it is desirable to optimize the particle size distribution of a graphite powder. For example, in the particle size distribution of the graphite powder called for by the laser diffraction method, it is good that 10% particle size of accumulation is 3 micrometers or more, 50% particle size of accumulation is more than 10micrometer, and 90% particle size of accumulation is 70 micrometers or less. This is from the following reasons.

[0081] First, when the pack density of a graphite powder is considered, it is desirable from the ability to fill up an electrode the graphite powder concerned being [direction] efficient and having given width of face to particle size distribution. Furthermore, it is more advantageous if particle size distribution are close to a normal distribution.

[0082] However, when the unusual situations, such as a surcharge, arise, and many graphite powders with a small particle size are contained in the negative electrode, there is an inclination for generation of heat to be promoted. For this reason, it is necessary to stop the number of graphite powders with a small particle size to some extent. Moreover, in case a lithium ion is inserted between the graphite layers of a negative electrode, a microcrystal expands abbreviation 10% and presses a positive electrode and separator in a cell. When many graphite powders with a big particle size are contained in the negative electrode at this time, the influence by expansion of such a microcrystal is large, and there is an inclination for initial failures, such as internal short-circuit, to become easy to happen, from a bird clapper at the time of initial charge. For this reason, you also have to stop the number of graphite powders with a big particle size to some extent from the point of avoiding an initial failure.

[0083] The particle size distribution of an above-mentioned graphite powder are set up in consideration of the influence of the particle size distribution to such a cell, and have become the form blended with sufficient balance from a graphite powder with a large particle size to a small graphite powder. If the graphite powder which has such particle size distribution is used as an active material of a negative electrode, while high electrode restoration nature will be obtained, in the unusual situations at the time of overcharge etc., it will be hard to produce generation of heat, and the initial failure by expansion of an electrode will be prevented, and the cell excellent in safety and reliability will be obtained. Furthermore, when 90% particle size of accumulation of a graphite powder is 60 micrometers or less, an initial failure will be reduced greatly and the reliability of a cell will improve further.

[0084] Moreover, in order to raise the heavy-loading property of a cell, it is desirable for the average of the disruptive strength of a graphite powder to be two or more [6.0 kgf(s)/mm].

[0085] That is, the ease of moving of the electrolyte ion at the time of electric discharge influences the load characteristic of a cell. For example, if a hole exists in an electrode mostly, the electrolytic solution will sink into the electrode concerned enough, and, as for a load characteristic, the moving state of electrolyte ion will be improved from a bird clapper good.

[0086] on the other hand -- graphite material -- a shaft orientations -- a carbon hex-steel side -- progressing -- **** -- the -- being piled up -- the microcrystal of c axis is realized And electrolyte ion is doped and ** doped among the layers of a heap of.

[0087] Since combination of such carbon hex-steel sides of graphite material is weak coupling called Van der Waals force, it is easy to deform here to stress. Therefore, the crevice between these carbon hex-steel sides has high possibility of being crushed in case it is pressed at the production process of a negative electrode, and, for this reason, it is difficult for graphite material to usually maintain a hole compared with nongraphitizing-carbon material. Therefore, it is desirable to sort out and use that in which a hole cannot be easily crushed by graphite material by regulating a disruptive strength. The average of an above-mentioned disruptive strength, i.e., the range or more [6 kgf(s)/mm] of two, is set up from this point, and it is using the graphite which has such a disruptive strength, a hole comes to be maintained in a negative electrode, and the cell excellent in the load characteristic is obtained.

[0088] In addition, the average of this disruptive strength is measured as follows. First, sample powder is observed with an optical microscope and zero l powder [as / whose length of a portion with the longest length is **10% of a mean particle diameter] is chosen. And about each 10 piece selected sample powder, the disruptive strength of a particle is measured applying a load and the average is computed.

[0089] As a graphite material used as a negative electrode, as long as it fulfills the above conditions, you may be the natural graphite produced as a mineral, and may be the artificial graphite compounded by carbonizing an organic material and carrying out high temperature processing further.

[0090] Each organic material illustrated as a start raw material of the scale-like graphite which serves as an electric conduction agent previously as an organic material which faces generating the above-mentioned artificial graphite and turns into a start raw material is usable. Moreover, you may apply to the conditions which also showed fundamentally the heat treatment conditions of an organic material used as a start raw material previously correspondingly. However, the detailed conditions at the time of generating the graphite which the property for which a negative-electrode active material is asked differs from the property for which an electric conduction agent is asked, and serves as a negative-electrode active material -- **** -- it is necessary to set up so that the conditions of crystallinity [like], true density, relative bulk density, a shape parameter x , specific surface area, particle size distribution, and a particle disruptive strength may be satisfied. In addition, although a negative electrode is presented with the obtained graphite material in the form pulverized and classified, it is desirable to perform pulverization before graphitization like between the temperature up process before and after carbonization and calcining or before graphitization.

[0091] However, when thinking especially relative bulk density and a disruptive strength as important and generating graphite material, it is good to produce a carbon-material molding object, to heat-treat this, and to perform graphitization.

[0092] With a carbon-material molding object, the corks used as a filler and the binder pitch used as a molding agent and a sintering agent are mixed and cast, and a binder pitch is carbonized by heat-treating this molding object (precursor of a carbon-material molding object). Graphitization is performed by infiltrating a melting pitch, carbonizing it and heat-treating it further at this carbon-material molding object. And the acquired graphitization molding object is pulverized and classified.

[0093] Here, since the graphite powder obtained by doing in this way pulverizes a graphite molding object with a high degree of hardness and is obtained, its relative bulk density is high, and its disruptive strength is strong. For this reason, compression molding -- facing -- that a hole is crushed **** -- charge and discharge -- facing -- a negative electrode -- it has not been said that the graphite powder concerned separates and falls from a mixture.

[0094] And in the generation process of this graphite, since the corks and the binder pitch which are a filler are used as the start raw material, it graphitizes as the polycrystalline substance, and at the time of heat treatment, sulfur and nitrogen which are further contained in a raw material serve as gas, and are generated, and, finally the path becomes a micro hole. Since, as for the graphite generated by having such a micro hole, the hole may also serve as a storing place of a lithium, the dope and ** dope reaction of a lithium tend to advance. Therefore, the negative electrode which consisted of such graphite powders will demonstrate the performance which was very excellent.

[0095] Moreover, the manufacture method manufactured from such a carbon molding object has industrially advantageous yield highly.

[0096] In addition, you may make it constitute the above-mentioned carbon molding object from a raw material which gave moldability and the degree of sintering to the filler itself.

[0097] Next, as the electrolytic solution used with a nonaqueous electrolyte rechargeable battery, the nonaqueous electrolyte which comes to dissolve an electrolyte in a non-aqueous solvent is used.

[0098] Although it will be the requisite as a non-aqueous solvent to use for the main solvent what have a comparatively high dielectric constant, such as ethylene carbonate (EC), it is the purpose which raises the transfer capacity and the low-temperature property of electrolyte ion, and it is desirable to use a hypoviscosity solvent together.

[0099] As a high dielectric constant solvent, propylene carbonate (PC) besides EC, butylene carbonate, vinylene carbonate, sulfolanes, butyrolactones, and valerolactones are suitable.

[0100] As a hypoviscosity solvent, symmetrical or unsymmetrical chain-like carbonates, such as diethyl carbonate, dimethyl carbonate, methylethyl carbonate, and methylpropyl carbonate, are suitable. Even if it mixes to a high dielectric constant solvent independently, you may mix these hypoviscosity solvent to a high dielectric constant solvent combining two or more kinds.

[0101] Here, in using graphite material especially for a negative electrode, it is cautious of selection of a high dielectric constant solvent. That is, when using graphite material for a negative electrode, as for PC, it is desirable for it to be necessary to avoid use, since it has graphite material and reactivity, and to use EC etc. as a main solvent. Moreover, the compound of the structure which replaced the hydrogen atom of EC by the halogen can also be used as a main solvent.

[0102] However, it is usable if the parts of the compound which replaced the hydrogen atom of EC used as the main solvent or EC by the halogen as 2nd component solvent are used for the grade which carries out little substitution even if there are graphite material and reactivity like PC. As this 2nd component solvent, butylene carbonate besides PC, 1, 2-dimethoxyethane, 1, 2-diethoxy methane, gamma-butyrolactone, a valerolactone, a tetrahydrofuran, 2-methyl tetrahydrofuran, 1, 3-dioxolane, 4-methyl, 1, 3-dioxolane, a sulfolane, a methyl sulfolane, etc. are mentioned. In addition, as for the addition of the component solvent of these 2nd, it is desirable to hold down to under 10 capacity %.

[0103] As an electrolyte which dissolves in a non-aqueous solvent, each thing usually used by this kind of cell is usable.

[0104] Specifically, LiPF_6 , LiClO_4 , LiAsF_6 , LiBF_4 , $\text{LiB}(\text{C}_6\text{H}_5)_4$, $\text{CH}_3\text{SO}_3\text{Li}$, $\text{CF}_3\text{SO}_3\text{Li}$, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and $\text{LiC}(\text{CF}_3\text{SO}_2)_3$, LiCl , LiBr , etc. are mentioned, and especially LiPF_6 is desirable. Moreover, even if it uses independently, you may use these electrolytes combining two or more kinds.

[0105]

[Example] The example of this invention is explained based on an experimental result.

[0106] The structure of the cell produced in each example of an experiment of the composition after-mentioned of the produced cell is shown in drawing 3.

[0107] As shown in drawing 3, this nonaqueous electrolyte rechargeable battery winds the negative electrode 1 which applies a negative-electrode active material to the negative-electrode charge collector 10, and becomes it, and the positive electrode 2 which comes to apply a positive active material to the positive-electrode charge collector 11 through separator 3, and comes to contain it with the cell can 5, where an insulator 4 is laid in the upper and lower sides of this winding object.

[0108] the aforementioned cell can 5 -- the cell lid 7 -- the obturation gasket 6 -- minding -- by closing, it is attached and connects with a negative electrode 1 or a positive electrode 2 electrically through the negative-electrode lead 12 and the positive-electrode lead 13, respectively, and it is constituted so that it may function as the negative electrode or positive electrode of a cell

[0109] And by the cell of this example, the aforementioned positive-electrode lead 13 is welded to the safe valve gear 8 which has a current breaker style, and is attached, and electrical installation with the cell lid 7 is planned through this safe valve gear 8 and the PTC element 9.

[0110] In the cell which has such composition, if the pressure inside a cell rises, the aforementioned safe valve gear 8 will be pushed up, and will deform. Then, the positive-electrode lead 13 leaves the safe valve gear 8 and the welded portion, and is cut, and current is intercepted.

[0111] The example of the one example experiment of an experiment examined the effect of using the mixture of a scale-like graphite and a fibrous graphite as an electric conduction agent of a positive electrode, about the case where nongraphitizing-carbon material is used as a negative-electrode active material.

[0112] First, the negative-electrode active material of a negative electrode 1 was compounded as follows.

[0113] To the furfuryl alcohol 100 weight section, the phosphoric acid 0.5 weight section and the water 10 weight section were mixed 85%, and the ***** polymer (furfuryl alcohol resin (PFA)) was obtained by heating this on a water bath for 5 hours. The temperature of 500 degrees C carbonized and ground the obtained furfuryl alcohol resin among the nitrogen air current in 5 hours after removing the water and unreacted alcohol which remained by vacuum distillation. And the temperature up of this pulverization object was carried out to 1200 degrees C, it was heat-treated for 1 hour, and the powder of the carbon material (nongraphitizing-carbon material) of 20 micrometers of mean particle diameters was obtained by grinding further. In addition, as a result of performing X diffraction measurement about this nongraphitizing-carbon material, the spacing of a field (002) was 0.383nm. Moreover, oxidization exoergic peak temperature [in / the differential thermal analysis in the inside of 1.52 g/cm³ and an air air current / in the true specific gravity by the pycnometer] was 634 degrees C.

[0114] Next, the negative electrode 1 was produced by making into a negative-electrode active material the nongraphitizing-carbon powder obtained by doing in this way.

[0115] first -- as the above-mentioned nongraphitizing-carbon powder 90 weight section and binding material -- the polyvinylidene-fluoride (PVDF) 10 weight section -- mixing -- a negative electrode -- a mixture -- preparing -- this negative electrode -- a mixture is distributed to N-methyl pyrrolidone used as a solvent -- making -- a negative electrode -- a mixture -- it considered as the slurry (the shape of a paste)

[0116] and this negative electrode -- a mixture -- after applying to both sides of the thickness 10micrometer band-like copper foil used as the negative-electrode charge collector 10 and making them dry a slurry, the band-like negative electrode 1 was produced by carrying out compression molding by the constant pressure

[0117] On the other hand, the positive active material of a positive electrode 2 was produced as follows.

[0118] One mol of cobalt carbonate was mixed with 0.5 mols of lithium carbonates, and it calcinated at the temperature of 900 degrees C among air for 5 hours. It was well in agreement with the peak of ** which performed X diffraction measurement about this obtained material, and LiCoO_2 registered into the JCPDS file.

[0119] Thus, obtained LiCoO_2 was ground so that 50% particle size of accumulation obtained by the laser diffraction method might be set to 15 micrometers.

[0120] Next, the positive electrode 2 was produced by making LiCoO_2 obtained powder into a positive active material.

[0121] First, the LiCoO_2 powder 95 weight section and the lithium-carbonate powder 5 weight section were mixed. and the polyvinylidene-fluoride 3 weight section used as 9l. weight section of this mixture, the mixture 6 weight section of the scale-like graphite (Lonza tradename KS- 15) used as an electric conduction agent, and fibrous carbon

{ tradename VGCF by Showa Denko K.K.), and binding material -- mixing -- a positive electrode -- the mixture was prepared In addition, each amount of mixtures of a scale-like graphite and fibrous carbon was changed as shown in Table 1. and this positive electrode -- a mixture is distributed to N-methyl pyrrolidone -- making -- a positive electrode -- a mixture -- it considered as the slurry (the shape of a paste)

[0122] and this positive electrode -- a mixture -- after applying and making both sides of a band-like aluminum foil with a thickness of 20 micrometers it is thin to the positive-electrode charge collector 11 dry a slurry uniformly, the band-like positive electrode 2 was produced by carrying out compression molding

[0123] As shown in drawing 1 , through the separator 3 which consists of a fine porosity polypropylene film with a thickness of 25 micrometers, the laminating of the band-like negative electrode 1 produced as mentioned above and the band-like positive electrode 2 was carried out to the order of a negative electrode 1, separator 3, a positive electrode 2, and separator 3, they were wound many times, and the swirl type electrode object with an outer diameter of 18mm was produced.

[0124] Then, the produced swirl type electrode object was contained with the iron cell can 5 which performed nickel plating, and the electric insulating plate 4 was arranged in these swirl formula electrode vertical both sides. And the positive-electrode lead 13 made from aluminum was drawn from the positive-electrode charge collector 11, it welded to the cell lid 7, the negative-electrode lead 12 made from nickel was drawn from the negative-electrode charge collector 10, and it welded to the cell can 5.

[0125] Thus, into the cell can 5 with which the swirl type electrode object was contained, the electrolytic solution which dissolved LiPF₆ at a rate of 1 mol/l into the amount mixed solvent of isochores of propylene carbonate and dimethyl carbonate was poured in. And fixed by closing ** through the ***** ROGASU blanket 6 which applied the front face for the cell can 5, and the safe valve gear 8, the PTC element 9 and the cell lid 7 which have a current breaker style with asphalt, the airtightness in a cell was made to hold, and diameter 18mm and the cylindrical nonaqueous electrolyte rechargeable battery with a height of 65mm were produced.

[0126] About the cell produced as mentioned above, it carried out by having repeated the charge-and-discharge cycle, and asked for the ratio (capacity maintenance factor) of the capacity of a 100 cycle eye to the capacity of a two-cycle eye.

[0127] In addition, the charge-and-discharge cycle examination was performed on the conditions of discharging to 2.75V by the 2000mA constant current, after charging by maximum charge voltage 4.2V and charging current 1A for 2.5 hours, the bottom of the environmental temperature of 25 degrees C, and.

[0128] The measured capacity maintenance factor is combined with the amount of mixtures of a scale-like graphite and a fibrous graphite, and is shown in Table 1. Moreover, the result which plotted the rate of the fibrous carbon to the whole electric conduction agent on the horizontal axis about the capacity maintenance factor is shown in drawing 4 .

[0129]

[Table 1]

| 鱗片状黒鉛 : 纖維状炭素 (重量部) (重量部) | 容量維持率 (%) |
|------------------------------|-----------|
| 6 : 0 | 88 |
| 5.5 : 0.5 | 89 |
| 5 : 1 | 83 |
| 4 : 2 | 95 |
| 3 : 3 | 94 |
| 2 : 4 | 91 |
| 1 : 5 | 85 |
| 0 : 6 | 80 |

[0130] By the used cell which made only the scale-like graphite the electric conduction agent, only 88% of capacity maintenance factor is obtained, and only 80% of capacity maintenance factor is obtained by the cell using only fibrous carbon as an electric conduction agent so that drawing 4 may show.

[0131] On the other hand, by the cell which transposed a part of electric conduction agent to fibrous carbon, a maximum of 95% of capacity maintenance factor is obtained.

[0132] This shows that it is effective to use the mixture of a scale-like graphite and fibrous carbon as an electric conduction agent, when improving the capacity maintenance factor of a cell.

[0133] However, when the mixing percentage of fibrous carbon is as small as 10 % of the weight, and the mixing percentage of fibrous carbon is conversely as large as 80 % of the weight, the improvement in a capacity maintenance factor is seldom found compared with the case where a scale-like graphite or fibrous carbon is independently used for

an electric conduction agent.

[0134] From this, the mixing percentage of a scale-like graphite and fibrous carbon is understood that 85:15-25:75 are suitable by the weight ratio.

[0135] The example of the two example experiment of an experiment examined the effect of using the mixture of a scale-like graphite and a fibrous graphite as an electric conduction agent of a positive electrode, about the case where a graphite is used as a negative-electrode material.

[0136] The cell was produced like the example 1 of an experiment except making into a negative-electrode active material the graphite powder generated as follows. In addition, the mixing percentage of the scale-like graphite in an electric conduction agent and fibrous carbon was changed as shown in Table 2.

[0137] The coal tar system pitch 30 weight section used as a binder was added to the coal system corks 100 weight section used as a filler, and it mixed at temperature abbreviation 100 degree C. And the precursor of a carbon molding object was obtained by carrying out compression molding of this mixture with a press.

[0138] Next, after heat-treating the precursor of this carbon molding object at the temperature not more than 1000 degree C and considering as a carbon-material molding object, the binder pitch which carried out melting at the temperature of 200 degrees C or less was infiltrated, and it heat-treated at the temperature not more than 1000 degree C. Then, this pitch sinking-in / baking process was repeated several times, and the carbon molding object was acquired. And the graphite powder was produced by using this carbon molding object as a graphitization molding object, and pulverizing and classifying it by heat-treating at the temperature of 2600 degrees C under an inert atmosphere.

[0139] In addition, as a result of performing X diffraction measurement about the obtained graphite powder, 0.337nm and C shaft microcrystal thickness of a field (002) of the spacing of a field (002) were 50.0nm. Moreover, a 2.23 g/c3 specific surface area [true specific gravity / by the pycnometer / xave / average shape-parameter / 0.83 g/cm3 and] / according / relative bulk density / to 10 and a BET adsorption method is 4.4m2/g. Furthermore, for 3l. . 2 micrometer and accumulation 10% particle size, 2.3 micrometers and 50% particle size of l accumulation are [a mean particle diameter / 29.5 micrometers and 90% particle size of accumulation of the particle size distribution by the laser diffraction method] 53.7 micrometers. Moreover, the average of a disruptive strength is 7.lkgf/mm2. In addition, relative bulk density, average shape-parameter xave, and the disruptive strength were measured as follows.

[0140] It asked for <relative-bulk-density measuring method> relative bulk density by the method indicated by JISK-1469. That is, the measuring cylinder of capacity 100cm3 which measured mass beforehand is made slanting, a spoon is used for this and sample powder 100cm3 are gradually supplied to it. And the mass of a measuring cylinder and the whole sample powder is measured by 0.1g of minimum scales, and the weight W of sample powder is found by deducting the mass of a measuring cylinder from the mass. Next, a cork stopper is made the measuring cylinder with which sample powder was thrown in, and the measuring cylinder of the state is dropped from a height of about 5cm 50 times to a rubber board. Consequently, since the sample powder in a measuring cylinder is compressed, the capacity V of the compressed sample powder is read. And relative bulk density (g/cm3) is computed by the following formula.

[0141] $D=W/VD$: Relative bulk density (g/cm3)

W: Mass of the sample powder in a measuring cylinder (g)

Capacity of the sample powder in the measuring cylinder after V:50 times fall (cm3)

< average shape-parameter xave measuring method: Observe SEM method > sample powder using SEM (scanning electron microscope), and choose ten powder [as / whose length L of a portion with the longest length is **30% of a mean particle diameter]. And about each ten selected sample powder, thickness [of a portion] T with the thinnest thickness, length [of a portion] L with the longest length, and length W of the direction which intersects perpendicularly with the major axis equivalent to depth were measured, it asked for configuration rose meter based on the following formula, and the average was computed. This average was set to average shape-parameter xave.

[0142] $x: (W/T) \times (L/T)$

x: shape-parameter T: -- powdered partial thickness L: with the thinnest thickness -- the length W: length <measuring method of the average of disruptive strength> disruptive strength of the direction which intersects perpendicularly with a powdered major axis of the powdered direction of a major axis was measured using the minute compression tester (tradename MCTM[by Shimadzu Corp.]- 500) First, sample powder is observed with the optical microscope of testing-machine attachment, and zero l powder [as / whose length of a portion with the longest length is **10% of a mean particle diameter] is chosen. And about each 10 piece selected sample powder, a load is added, the disruptive strength of a particle is measured and the average is computed. Let this computed average be the average of a disruptive strength.

[0143] About the cell produced as mentioned above, it carried out by having repeated the charge-and-discharge cycle, and asked for the ratio (capacity maintenance factor) of the capacity of a 100 cycle eye to the capacity of a two-cycle eye. The measurement result of a capacity maintenance factor is combined with the amount of mixtures of a scale-like graphite and a fibrous graphite, and is shown in Table 2. Moreover, the result which plotted the rate of the fibrous

carbon to the whole electric conduction agent on the horizontal axis about the capacity maintenance factor is shown in drawing 5.

[0144]

[Table 2]

| 鱗片状黒鉛 : 繊維状炭素 (重量部) (重量部) | 容量維持率 (%) |
|------------------------------|-----------|
| 6 : 0 | 80 |
| 5.5 : 0.5 | 81 |
| 5 : 1 | 82 |
| 4 : 2 | 90 |
| 3 : 3 | 91 |
| 2 : 4 | 88 |
| 1 : 5 | 78 |
| 0 : 6 | 70 |

[0145] By the used cell which made only the scale-like graphite the electric conduction agent, only 80% of capacity maintenance factor is obtained, and only 70% of capacity maintenance factor is obtained by the cell using only fibrous carbon as an electric conduction agent so that drawing 5 may show.

[0146] On the other hand, by the cell which transposed a part of electric conduction agent to fibrous carbon, a maximum of 91% of capacity maintenance factor is obtained.

[0147] This shows that the effect by using the mixture of a scale-like graphite and fibrous carbon as an electric conduction agent is more notably demonstrated when using a graphite as a negative-electrode active material.

[0148] However, when the mixing percentage of fibrous carbon is as small as 10 % of the weight, and the mixing percentage of fibrous carbon is conversely as large as 80 % of the weight, the improvement in a capacity maintenance factor is seldom found compared with the case where a scale-like graphite or fibrous carbon is independently used for an electric conduction agent.

[0149] From this, when using a graphite as a negative-electrode material, the mixing percentage of a scale-like graphite and fibrous carbon is understood that 85:15-25:75 are suitable by the weight ratio.

[0150] the example of the three example experiment of an experiment -- a positive electrode -- the ratio of the electric conduction agent which a mixture is made to contain was examined

[0151] a positive electrode -- the nonaqueous electrolyte rechargeable battery was produced like the example 2 of an experiment except having changed the mixture of the LiCoO₂ powder and lithium-carbonate powder of a mixture, a scale-like graphite, fibrous carbon, and the amount of mixtures of a polyvinylidene fluoride, as shown in Table 3

[0152] About the produced cell, it carried out by having repeated the charge-and-discharge cycle, and asked for the ratio (capacity maintenance factor) of the capacity of a 100 cycle eye to the capacity of a two-cycle eye. the capacity of a two-cycle eye, and the measurement result of a capacity maintenance factor -- a positive electrode -- it combines with composition of a mixture and is shown in Table 3 moreover -- a capacity maintenance factor -- a positive electrode -- a mixture -- the result which plotted the rate of the electric conduction agent (a scale-like graphite and fibrous carbon) to the whole on the horizontal axis -- drawing 6 -- the capacity of a two-cycle eye -- a positive electrode -- a mixture -- the result which plotted the rate of the electric conduction agent to the whole on the horizontal axis is shown in drawing 7

[0153]

[Table 3]

| LiCoO ₂ と炭酸リチウムの混合物 (重量部) | 鱗片状 黒鉛 (重量部) | 繊維状 炭素 (重量部) | 結着剤 (重量部) | 2サイクル目 容量 (mAh) | 容量 維持率 (%) |
|---|--------------------|--------------------|--------------|-----------------------|------------------|
| 91 | 3 | 3 | 3 | 1425 | 91 |
| 93 | 2 | 2 | 3 | 1440 | 88 |
| 87 | 5 | 5 | 3 | 1450 | 90 |
| 81 | 8 | 8 | 3 | 1421 | 89 |
| 95 | 1 | 1 | 3 | 1380 | 60 |
| 73 | 12 | 12 | 3 | 1290 | 84 |

[0154] drawing 6 and drawing 7 show -- as -- the capacity of a capacity maintenance factor and a two-cycle eye -- a positive electrode -- a mixture -- the electric conduction agent to the whole is comparatively alike, and it depends, and

changes And about all, when [of an electric conduction agent] it is comparatively less than 3 % of the weight or is over 16 % of the weight conversely, sufficient value is no longer acquired. the positive electrode from this -- a mixture -- the rate of the electric conduction agent to the whole is understood that 3 - 16 % of the weight is suitable
[0155] In the example of the four example experiment of an experiment, the kind of fibrous carbon mixed to an electric conduction agent was changed, and each effect was compared.

[0156] a positive electrode -- the nonaqueous electrolyte rechargeable battery was produced like the example 2 of an experiment except having changed the kind of fibrous carbon, as it fixed to 4 % of the weight and 2% of the weight, respectively and the amount of mixtures of a scale-like graphite and fibrous carbon was shown in Table 4 in a mixture In addition, the used fibrous carbon is a VGCF carbonization article (Showa Denko K.K. make), glass car carbonization article GWV-1A (Nikkiso Co., Ltd. make), glass car graphitization article GWH-1A (Nikkiso Co., Ltd. make), and four kinds of T-300 (Toray Industries, Inc. make).

[0157] About the produced cell, it carried out by having repeated the charge-and-discharge cycle, and asked for the ratio (capacity maintenance factor) of the capacity of a 100 cycle eye to the capacity of a two-cycle eye. The measurement result of a capacity maintenance factor is shown in Table 4 with the kind of fibrous graphite. Moreover, the capacity maintenance factor of the cell which used a scale-like graphite independent for the electric conduction agent, and produced it as comparison is also collectively shown in Table 4.

[0158]

[Table 4]

| 繊維状炭素 | 容量維持率 (%) |
|-----------------|--------------|
| VGCF炭素化品 | 89 |
| グラスカー炭素化品GWV-1A | 89 |
| グラスカー黒鉛化品GWH-1A | 90 |
| T-300 | 88 |
| 繊維状炭素なし | 80 |

[0159] As shown in Table 4, compared with the cell by which the cell using the mixture of a scale-like graphite and fibrous carbon as an electric conduction agent used a scale-like graphite independent for the electric conduction agent, a capacity maintenance factor with big all is obtained.

[0160] From this, the effect by mixing fibrous carbon to an electric conduction agent not depending on the kind of fibrous carbon, but being demonstrated was checked.

[0161]

[Effect of the Invention] With the nonaqueous electrolyte rechargeable battery of this invention, since the mixture of a scale-like graphite and fibrous carbon is used as an electric conduction agent of a positive electrode, even when it uses on heavy-loading electric discharge conditions, the electrode structure of a positive electrode is not destroyed, but a long cycle life is acquired, so that clearly also from the above explanation. Therefore, this invention can greatly contribute to improvement in the practicality of a nonaqueous electrolyte rechargeable battery.

[Translation done.]